...CE OF NAVAL RESEARCH

Contract N00014-82-0280

Task No. NR413E001

TECHNICAL REPORT NO. 46

Atomic Hydrogen- A Reagent for the Extraction of Chemical Species from Silicon Surfaces

by

J.T. Yates, Jr., C.C. Cheng, Q. Gao, M.L. Colaianni, and W.J. Choyke

Submitted to

2nd International Symposium
on Atomic Layer Epitaxy
Session E-12

Surface Science Center
Department of Chemistry
University of Pittsburgh
Pittsburgh, PA 15260

June 1, 1992

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

MASTER COPY - FOR REPRODUCTION PURPOSES

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: 46
2. GOVT ACCESSION NO.:
3. RECIPIENT'S CATALOG NUMBER:

4. TITLE (and Subtitle): Atomic Hydrogen- A Reagent for the Extraction of Chemical Species from Silicon Surfaces
5. TYPE OF REPORT & PERIOD COVERED: Preprint
6. PERFORMING ORG. REPORT NUMBER:

7. AUTHOR(s): J.T. Yates, Jr., C.C. Cheng, Q. Gao, M.L. Colaianni, and W.J. Choyke
8. CONTRACT OR GRANT NUMBER(s):

9. PERFORMING ORGANIZATION NAME AND ADDRESS: Surface Science Center, Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260
10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS:

11. CONTROLLING OFFICE NAME AND ADDRESS:
12. REPORT DATE: June 1, 1992
13. NUMBER OF PAGES:

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office):
15. SECURITY CLASS. (of this report): Unclassified
15a. DECLASSIFICATION/DOWNGRADING SCHEDULE:

16. DISTRIBUTION STATEMENT (of this Report):

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report):

18. SUPPLEMENTARY NOTES:

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Silicon
halogens
Eley-Rideal reactive
Atomic hydrogen
Extraction
Atomic layer epitaxy

20. ABSTRACT (Cont

The surface chemistry of adsorbed halogen atoms on Si(100) has been studied using several surface science methods. It has been found that Cl atoms bond to dangling bonds on symmetric Si_2 dimer sites, and that the Si-Cl bond angle is tilted from the normal in the vertical plane containing the Si_2 dimer bond. The covalently-bonded halogens Cl, Br, and I have been studied on Si(100) using atomic hydrogen bombardment at low substrate temperatures (300 - 630 K). In all cases, facile elimination of the hydrogen halide occurs, and the coverage of halogen may be driven to zero by moderate exposure to atomic hydrogen. The halogen extraction process is almost non-activated, suggesting that the chemical reaction to produce hydrogen halide species is driven by the potential energy carried by the atomic hydrogen species. This is an example of an Eley-Rideal reaction process and provides a potentially useful new approach for controlling atomic layer chemistry on semiconductors.

DD FORM 1 JAN 73 1473

PAGE (When Data Entered)

Submitted to: 2nd International Symposium
on Atomic Layer Epitaxy
Session E-3

Date: 1 June 1992

ATOMIC HYDROGEN- A REAGENT FOR THE EXTRACTION OF CHEMICAL SPECIES FROM SILICON SURFACES

John T. Yates, Jr., C.C. Cheng, Q. Gao,
M.L. Colaianni, and W.J. Choyke

Surface Science Center
Department of Chemistry
University of Pittsburgh
Pittsburgh, PA 15260

412-624-8320

ATOMIC HYDROGEN- A REAGENT FOR THE EXTRACTION OF CHEMICAL SPECIES FROM SILICON SURFACES

John T. Yates, Jr., C.C. Cheng, Q. Gao,
M.L. Colaianni, and W.J. Choyke

Surface Science Center
Department of Chemistry
University of Pittsburgh
Pittsburgh, PA 15260

Abstract

The surface chemistry of adsorbed halogen atoms on Si(100) has been studied using several surface science methods. It has been found that Cl atoms bond to dangling bonds on symmetric Si_2 dimer sites, and that the Si-Cl bond angle is tilted from the normal in the vertical plane containing the Si_2 dimer bond. The covalently-bonded halogens Cl, Br, and I have been studied on Si(100) using atomic hydrogen bombardment at low substrate temperatures (300 - 630 K). In all cases, facile elimination of the hydrogen halide occurs, and the coverage of halogen may be driven to zero by moderate exposure to atomic hydrogen. The halogen extraction process is almost non-activated, suggesting that the chemical reaction to produce hydrogen halide species is driven by the potential energy carried by the atomic hydrogen species. This is an example of an Eley-Rideal reaction process and provides a potentially useful new approach for controlling atomic layer chemistry on semiconductors.

Atomic hydrogen driven extraction of adsorbed methyl (CH_3) species on Si(100) is also observed to occur with lower efficiency than halogen extraction. Thermal desorption studies indicate that the carbon extraction process occurs as the result of atomic hydrogen-induced etching of the surface, producing gas phase alkyl silanes such as CH_3SiH_3.

I. Introduction

The development of low temperature surface processes to manipulate adsorbed species on semiconductor surfaces provides the basis for new methods to produce heterostructure semiconductor devices. Our knowledge of the fundamentals governing chemistry on semiconductor surfaces is in its infancy, and mechanistic understanding of elementary semiconductor surface processes is needed[1]. In this paper, two new classes of surface reactions involving atomic hydrogen as a reagent are described. It is anticipated that the principles governing these two types of atomic hydrogen-driven surface chemistries will find application in a wide range of semiconductor surface processes.

II. Experimental Details

The ultrahigh vacuum apparatus and methods used for this research have been described previously[2]. The methods employed include temperature programmed desorption(TPD), Auger electron spectroscopy(AES), high resolution electron energy loss spectroscopy(HREELS), and digital ESDIAD[3]. Adsorbate gases are adsorbed on the single crystal surface using collimated molecular beam dosers which deliver an absolutely known flux of gas,

permitting quantitative exposures and uptake measurements to be made[4].

III. Results and Discussion

A. Structure of Chemisorbed Cl on Si(100)-(2 x 1)

Figure 1 shows a schematic diagram of the digital ESDIAD apparatus employed for this work[3]. An electron beam excites surface species on the Si(100) single crystal, producing beams of positive ions which are spatially detected by the microchannelplate detector system. The pattern of ion emission angles is closely related to the direction of the surface chemical bonds which are ruptured by the electronic excitation process[5]. These ion emission directions are modified by final state image and reneutralization effects[6], as well as by the electrical bias applied to the crystal for pattern compression. Because the ion emission dynamics are governed by rapid Franck-Condon excitation from the ground state to a repulsive upper state, the statistical summation of millions of ion emission directions from an ensemble of adsorbate species on a single crystal will provide a statistical measurement of the distribution of chemical bond angles caused by thermal disorder at the measurement temperature. This permits digital ESDIAD to be

used also as a powerful tool for the study of the dynamical behavior of adsorbates[5].

Figure 2 shows a sequence of Cl^+ ESDIAD patterns from chlorine adsorption on Si(100)-(2 x 1)[7,8]. At an adsorption temperature of 120 K, a normal Cl^+ beam is observed to overlap an underlying Cl^+ pattern exhibiting four-fold symmetry. Upon annealing the chlorine-covered surface to temperatures above 120 K, the central Cl^+ beam is seen to disappear, revealing the inclined beams which become more pronounced. This process culminates at about 673 K. We believe that the normal Cl^+ beam is caused by a minority of adsorbed Cl atoms which bridge the symmetric Si dimer sites. These species have a high cross section for ESD production of Cl^+, and the normal emission from these bridged-Cl species therefore dominates the low temperature ESDIAD pattern. As the system is heated, the bridged-Cl species convert to single-bonded Cl species, with the inclined Si-Cl bonds oriented in the vertical plane which includes the [011] crystallographic axis. This azimuthal plane corresponds to the Si-Si bond directions in the Si_2 surface dimers on a Si(100) terrace. The orthogonal Si-Cl beam directions correspond to inclined Si-Cl bonds on the mixture of two types of crystal terraces present on the slightly misaligned Si(100) crystal.

Figure 3 shows the vibrational behavior of the surface as a chlorine layer is heated over the same

temperature range as used in the ESDIAD experiments[8]. At 100 K, two Cl-related vibrational modes are observed at 600 cm^{-1} and at about 300 cm^{-1}. The 600 cm^{-1} mode is due to the Si-Cl stretching mode of the inclined Si-Cl bonds. Its frequency and intensity remains almost constant as the heating process occurs. The weak mode at about 300 cm^{-1} is assigned to a bridging-Cl species, linked between two Si atoms in a dimer pair on the Si(100)-(2 x 1) surface. The good analogy to the vibrational frequency of bridging-Cl in compounds such as Al_2Cl_6 was employed to make this assignment[9]. The vibrational behavior suggests that the bridging-Cl species is a minority species, since the intensity of the 600 cm^{-1} mode does not vary significantly during the heating process as the 300 cm^{-1} mode decreases in intensity. The bridging-Cl species is metastable with respect to the inclined Si-Cl species, which is the most stable species on Si(100). Similar behavior was observed in the theoretical calculations of Wu and Carter[10] for F on Si(100), except that an energy barrier for the bridge-to-inclined Si-F structure was not predicted theoretically. The large change observed in the Cl^+ ESDIAD pattern for the heating range 100 K - 673 K is related to the high ESD cross section for Cl^+ production from the small surface coverage of bridged-Cl which exists below 673 K.

B. Facile Extraction of Chemisorbed Halogen Atoms by Atomic Hydrogen

The Si-Cl bond may be broken easily by bombarding the surface with atomic hydrogen, produced on a hot tungsten filament in the ultrahigh vacuum system containing a low pressure of molecular hydrogen[11]. Figure 4 shows the behavior of the Cl surface coverage, along with similar measurements made for adsorbed Br and adsorbed I on Si(100). These measurements have been made in a way in which the small effect of the Auger electron beam on the halogen coverage has no effect on the interpretation. The fitted curves are best fits to first-order kinetics in halogen surface coverage at a surface temperature of 300 K. It is seen that the relative rate of halogen extraction is I > Br > Cl. A similar trend has been observed in gas phase studies for the reaction of atomic hydrogen with the methyl halides to produce hydrogen halide species[12].

The bromine extraction rate was studied as a function of the pressure of H_2 used in the chamber, as seen in Figure 5. The flux of atomic hydrogen is known to be proportional to the H_2 pressure under these conditions[13]. As the hydrogen pressure is increased, the rate of Br extraction increases at a surface temperature of 430 K; the inset shows that the Br

extraction rate is linearly proportional to the atomic H flux employed.

The temperature dependence of the atomic-H induced extraction of bromine was measured as shown in Figure 6. An activation energy for this process of only 1.6 ± 0.2 kcal/mol was measured over the range 300 K - 630 K, as shown in the inset to Figure 6. Similar studies of the kinetics of extraction of adsorbed Cl gave an activation energy of 2.1 ± 0.2 kcal/mol for Cl/Si(100). These low activation energies are indicative that the thermal excitation of the surface species is of little importance in governing the rate of the halogen extraction process.

Considered together, the kinetic behavior of the halogen extraction process induced by atomic hydrogen corresponds to the well known, but infrequently observed, Eley-Rideal kinetic process[11]. The process involves the use of the potential energy carried by the atomic H to produce the active complex involved in the removal of surface halogen. An active complex, Si...X...H is produced when atomic H collides with the covalently-bonded halogen atom, X. Accomodation of the incoming H atom by the silicon surface is not required in this mechanism. The potential energy of the atomic hydrogen is 52 kcal/mol compared to 1/2 $H_2(g)$, and this energy is the primary driver for the halogen extraction process observed.

The Eley-Rideal process observed for atomic hydrogen as a reagent is potentially important for a wide range of

surface chemistry. Other gas phase free radical species may be expected to be active in similar extraction processes on surfaces, and we will have to await future experiments before knowing the full implications of these first observations involving the most simple free radical species, atomic hydrogen. In particular, the use of atomic hydrogen extraction procedures for removal of surface halogen ligands (present in atomic layer epitaxy processes involving monolayers of group IV halide species) is expected to be of importance.

C. Extraction of Adsorbed Methyl Groups with Atomic Hydrogen

The chemisorption of methyl iodide, CH_3I, on Si(100) has been shown to be an efficient way to produce surface methyl groups which are stable up to about 600 K[14,15]. Therefore, we have employed CH_3I as a source of CH_3(a), and have studied the effect of bombardment by atomic hydrogen of the covalently-bonded CH_3 groups. Figure 7 shows the surface temperature dependence of the rate of removal of carbon (as CH_3(a) species) by means of bombardment by atomic hydrogen. Compared to the exposures needed for halogen extraction (Figure 3), atomic hydrogen is much less effective in removing methyl groups from the surface. In addition, the temperature dependence of the rate of the methyl extraction process is opposite to that

seen for the halogen extraction process. In the case of methyl extraction, the rate decreases above a surface temperature of about 450 K.

Thermal desorption studies show that $CH_3SiH_3(g)$ is evolved following atomic hydrogen bombardment of $CH_3(a)$[15]. In addition, $SiH_4(g)$ is also evolved in the same temperature range near 600 K. The loss of surface methyl therefore occurs as a result of atomic hydrogen etching of the Si(100) surface. The decrease in rate above about 450 K is caused by the reduction in the capacity of the surface to adsorb hydrogen at this temperature, and hence to the reduced rate of etching above 450 K.

The comparative rate of removal of surface methyl groups and surface iodine atoms by atomic hydrogen bombardment is also easily seen in Figure 8, where the vibrational characterization is shown. The vibrational spectrum shows modes related to both the Si-I bond and to the $CH_3(a)$ species produced from dissociative adsorption of CH_3I. Atomic hydrogen efficiently removes the adsorbed iodine Si-I groups first, as seen by the preferential loss of υ(SiI) intensity.

IV. Summary

This brief review of the use of atomic hydrogen as a reagent for inducing surface reactions on silicon has dealt with two entirely different types of elementary surface processes.

1. Covalently-bonded halogen atoms may be efficiently removed by atomic hydrogen via an Eley-Rideal process yielding volatile hydrogen halide species. The rate of the Eley-Rideal process is almost temperature independent, indicating that thermal activation from the substrate is of little importance compared to the activation induced by the potential energy of the incident atomic hydrogen itself.
2. Covalently-bonded methyl groups are not readily removed from Si(100) by atomic hydrogen to produce methane. Instead, etching of the silicon surface to produce species such as CH_3SiH_3 and SiH_4 is the dominant route for methyl removal.
3. These two types of extraction processes may be useful in many materials processes such as atomic layer epitaxy.

V. Acknowledgement

We thank the Office of Naval Research for full support of this work.

VI. References

[1] M.E. Gross, J.M. Jasinski and J.T. Yates, Jr., Eds., "Chemical Perspectives of Microelectronic Materials," Vol. 131, Materials Research Society Symposium Proceedings.

[2] a) C.C. Cheng, R.M. Wallace, P.A. Taylor, W.J. Choyke and J.T. Yates, Jr., J. Appl. Phys., 67, 3693 (1990); b) M.J. Bozack, L. Muehlhoff, J.N. Russell, Jr., W.J. Choyke and J.T. Yates, Jr., J. Vac. Sci. Technol., A5, 1 (1987).

[3] J.T. Yates, Jr. M.D. Alvey, K.W. Kolasinski and M.J. Dresser, Nuclear Instrumentation and Methods in Physics Research, B27, 147 (1987).

[4] C.C. Cheng, R.M. Wallace, P.A. Taylor, W.J. Choyke and J.T. Yates, Jr., J. Appl. Phys., 67, 3693 (1990).

[5] a) J.T. Yates, Jr., M.D. Alvey, M.J. Dresser, M.A. Henderson, M. Kiskinova, R.D. Ramsier and Z. Szabó, Science, 255, 1397 (1992); b) R.D. Ramsier and J.T. Yates, Jr., Surf. Sci. Reports, 12, 243 (1991).

[6] a) Z. Miskovic, J. Vulkanic and T.E. Madey, Surf. Sci., 141, 285 (1984); b) Z. Miskovic, J. Vulkanic and T.E. Madey, Surf. Sci., 169, 405 (1986).

[7] C.C. Cheng, Q. Gao and J.T. Yates, Jr., in preparation.

[8] Q. Gao, C.C. Cheng and J.T. Yates, Jr., in preparation.

[9] E. Maslowsky, "Vibrational Spectra for Organometallic Compounds," John Wiley and Sons, Inc., 1977, New York, p. 61.

[10] a) C.J. Wu and E. Carter, J. Amer. Chem. Soc., 113, 9061 (1991); b) C.J. Wu and E. Carter, Phys. Rev. B 45, 9065 (1992); c) P.C. Weakliem, C.J. Wu and E. Carter, Phys. Rev. Lett., in press.

[11] C.C. Cheng, S.R. Lucas, H. Gutleben, W.J. Choyke and J.T. Yates, Jr., J. Amer. Chem. Soc., 114, 1249 (1992).

[12] a) W.E. Jones and J.L. Ma, Can. J. Chem., 64, 2192 (1986); b) A.A. Westenberg and N. deHaas, J. Chem. Phys., 62, 3321 (1975).

[13] a) D. Brennen and P.C. Fletcher, Proc. Roy. Soc. London, Ser. A, 250, 389 (1959); b) J.N. Smith, Jr. and W. Fite, J. Chem. Phys., 37, 898 (1962).

[14] H. Gutleben, S.R. Lucas, C.C. Cheng, W.J. Choyke and J.T. Yates, Jr., Surf. Sci., 257, 146 (1991).

[15] C.C. Cheng, S.R. Lucas, H. Gutleben, W.J. Choyke and J.T. Yates, Jr., Surf. Sci. Letters, in press.

Figure Captions

Figure 1. Digital ESDIAD apparatus for imaging chemical bond directions in adsorbed species.

Figure 2. ESDIAD patterns of Cl^+ from Si(100) as a function of annealing temperature. The initial Cl coverage is near 1 ML.

Figure 3. HREELS study of the spectral changes as a function of annealing temperature.

Figure 4. Atomic hydrogen extraction for halogen adsorbates from Si(100).

Figure 5. Hydrogen pressure dependence of Br extraction rate from Si(100).

Figure 6. Temperature Dependence of Br extraction rate from Si(100).

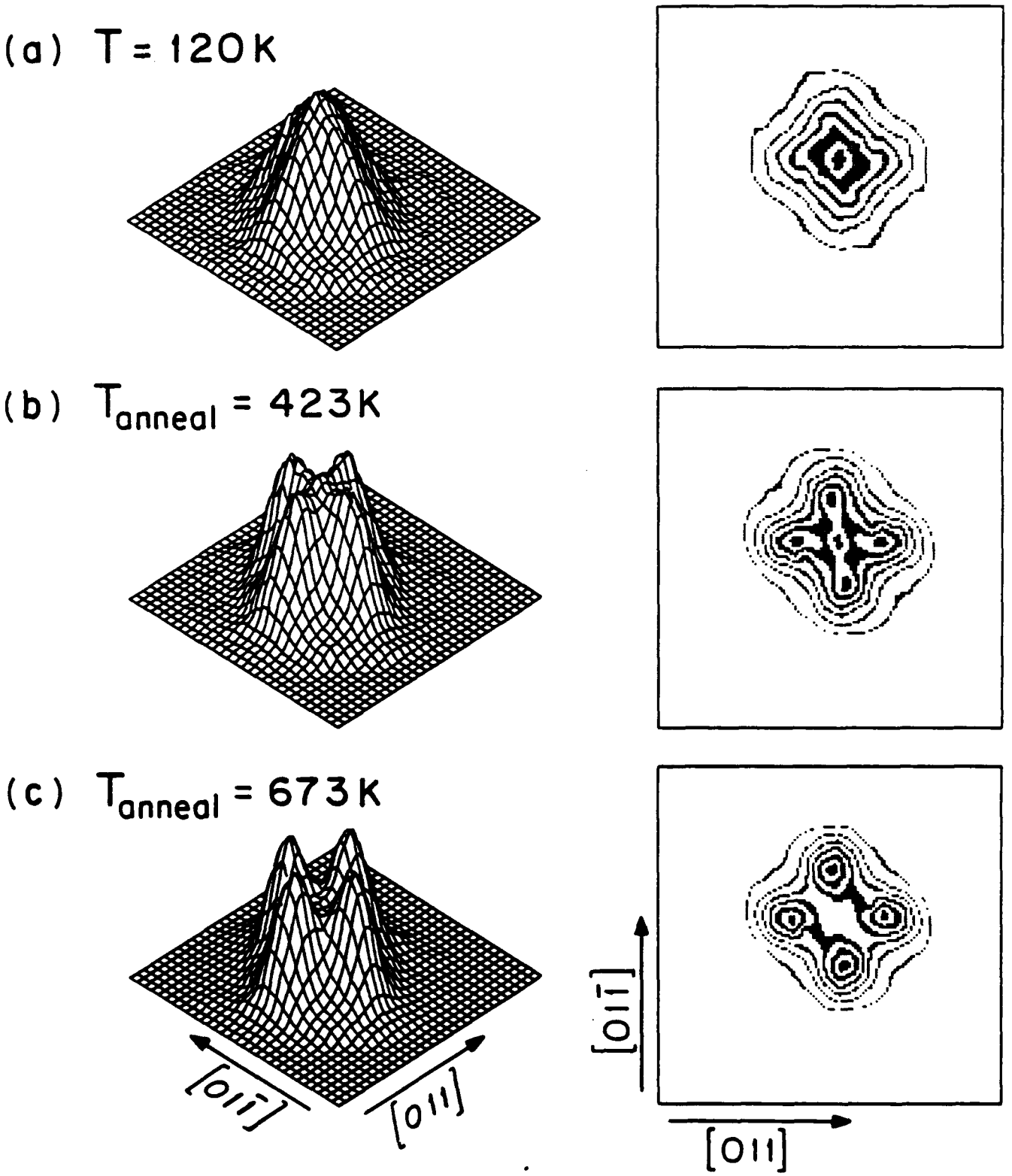
Figure 7. Temperature dependence of carbon removal from CH_3/Si(100) by atomic hydrogen.

Figure 8. HREELS study of atomic hydrogen extraction of iodine from Si(100). T = 585 K.

Yates, et al.

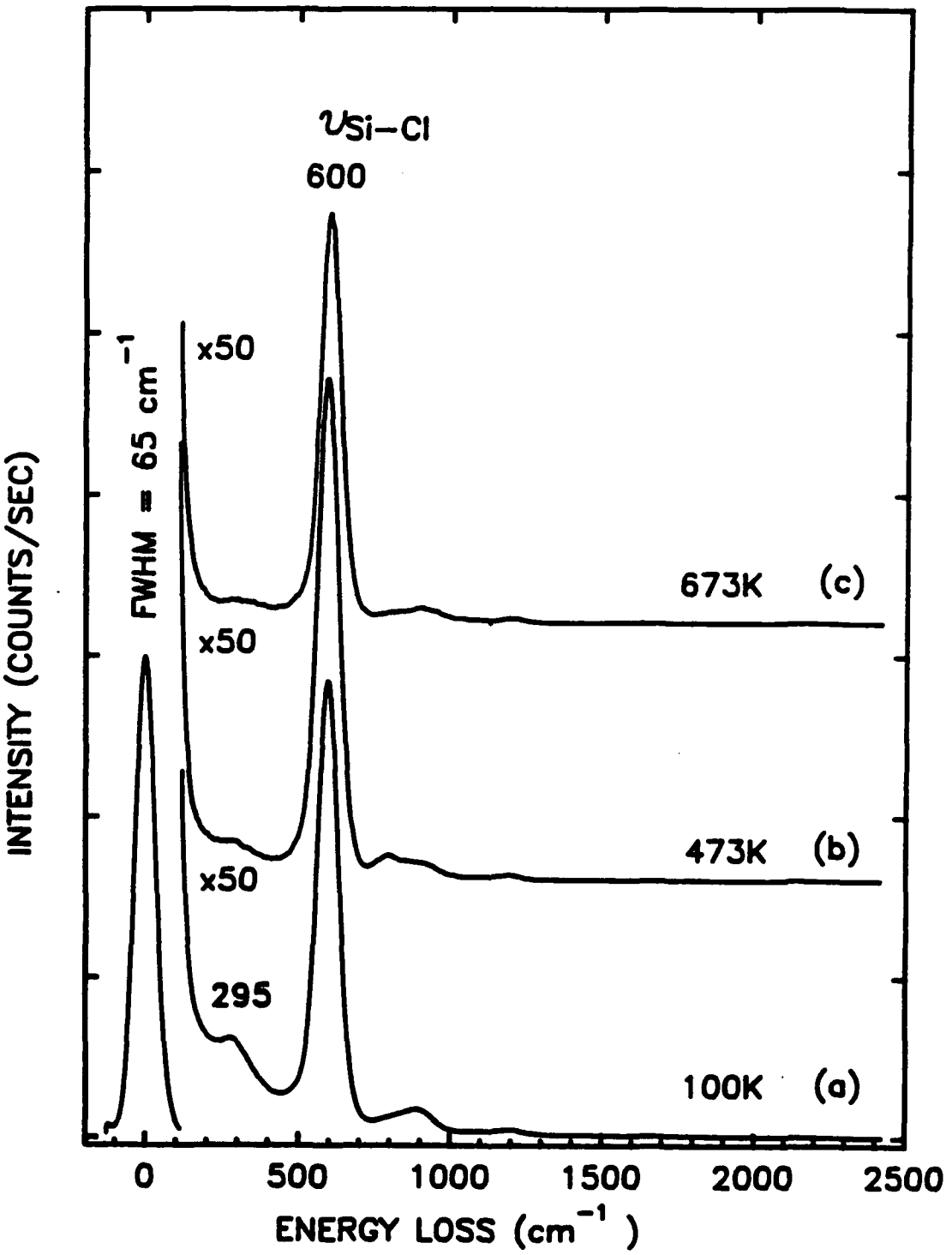
Figure 1

ESDIAD Patterns of Cl on Si(100)



Yates, et al.

Figure 2



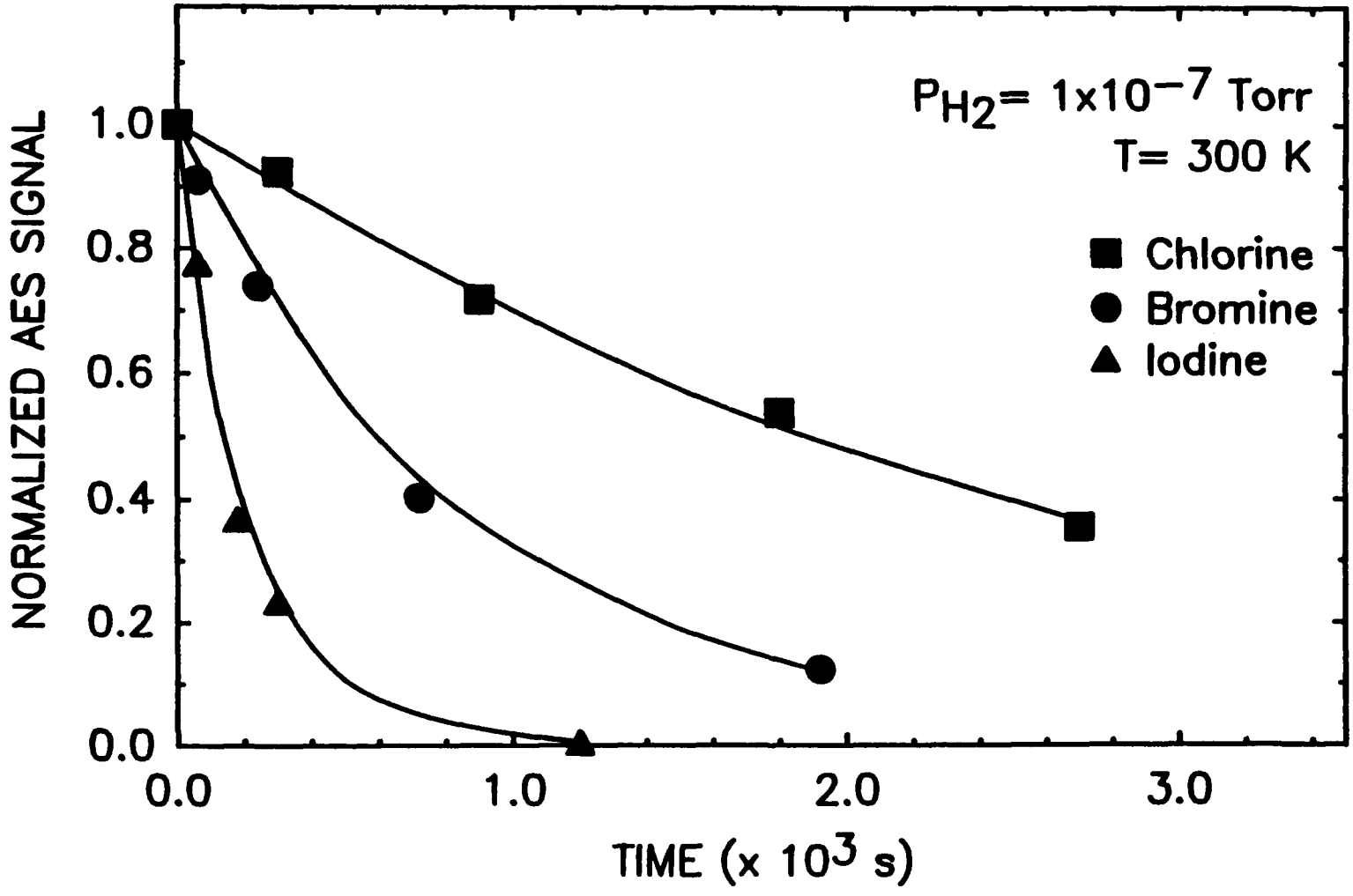
Yates, et al.

Figure 3

Yates, et al.

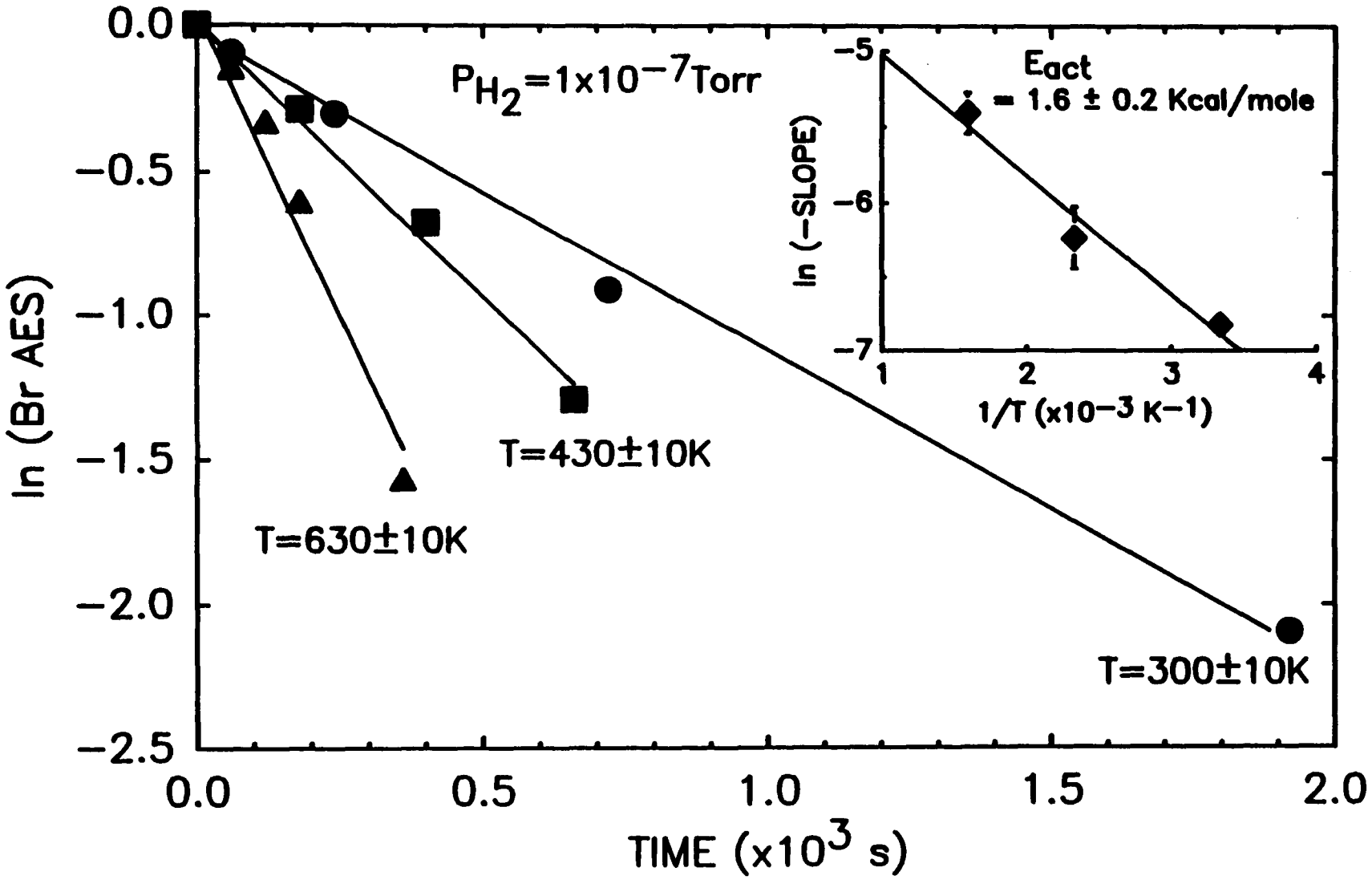
Figure 4

ATOMIC HYDROGEN EXTRACTION OF HALOGEN ADSORBATES ON Si(100)



Yates, et al.

Figure 5

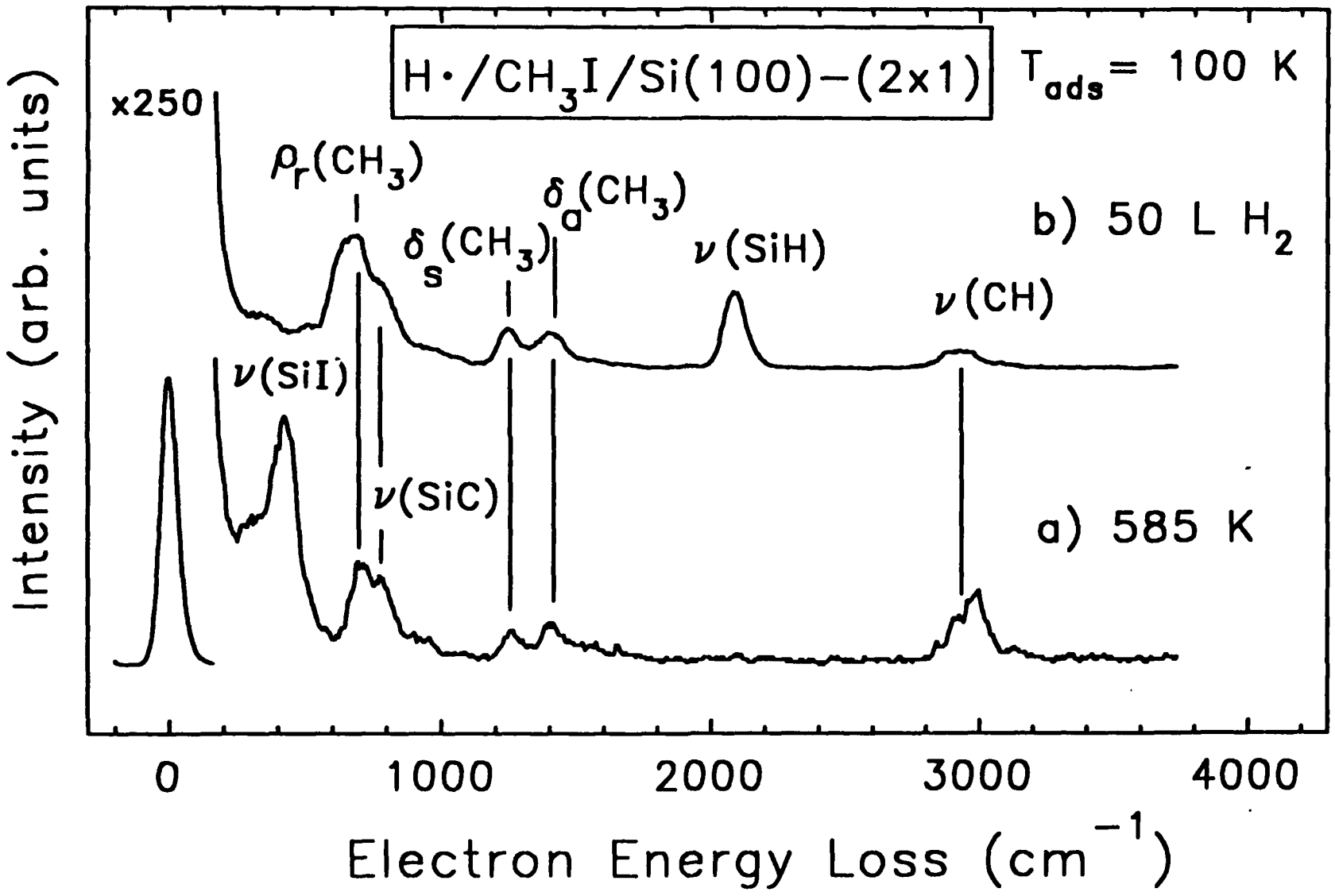


Yates, et al.

Figure 6

Figure 17

Atomic H Extraction of Adsorbed Iodine



Raleigh, NC 27695-7907
Tel: (919) 515-2377/3272
FAX: (919) 515-3419
e-mail: davis@mte.ncsu.edu

Prof. Salah Bedair 1
Department of Electrical Engineering
N.C.S.U.; Box
Raleigh, NC 27695
Tel: (919) 515-2336
e-mail: jll@@ecegrad.ncsu.edu

Max N. Yoder 1
ONR Code 1114
Arlington, VA 22217
Tel: (703) 696-4218
FAXes (703) 696-2611/3945/5383
e-mail: yoder@charm.isi.edu

Dr. A. M. Goodman 1
ONR, Code 1114
Arlington, VA 22217
Tel: (703) 696-4218
FAXes (703) 696-2611/3945/5383
e-mail: goodman@ocnr-hq.navy.mil

Dr. J. Pazik 1
ONR Code 1113
Arlington, VA 22217
Tel: (703) 696-4410
FAXes (703) 696-2611/3945/5383
e-mail: pazik@ocnr-hq.navy.mil
pazik%estd.decnet@ccf.nrl.navy.mil

Prof. J. T. Yates, Jr. 1
Dept. of Chemistry
Surface Science Ctr.
University of Pittsburgh
Pittsburgh, PA 15260
Tel: (412) 624-8320
FAX: (412) 624-8552
e-mail: yates@vms.cis.pitt.edu

Robert J. Markunas, R.A. Rudder 1
Research Triangle Institute; Box 12194
Research Triangle Park, NC 27709-2194
Tel: (919) 541-6153
FAX: (919) 541-6515
e-mail: rjmk@rti.rti.org

Professor Mark P. D'Evelyn 1
William Marsh Rice University
Dept. of Chemistry
P.O. Box 1892
Houston, TX 77251
Tel: (713) 527-8101, ext. 3468
FAX: (713) 285-5155
e-mail: mpdev@@langmuir.rice.edu

Dr. Howard K. Schmidt 1
Schmidt Instruments, Inc.
2476 Bolsover, Suite 234
Houston, TX 770054
Tel: (713) 529-9040

FAX: (713) 529-1147
e-mail: hksionwk@ricevm1.rice.edu

Prof. A. F. Tasch 1
Dept. of Electrical Engr. & Computer Science
Engineering Science Bldg.
University of Texas at Austin
Austin, TX 78712
Tel:
FAX:
e-mail: tasch@roz.ece.utexas.edu

Prof. Charles Tu 1
Dept of Electrical & Computer Engr.
UCSD
LaJolla, CA
Tel: (619) 534-4687
FAX: (619) 534-2486
e-mail: cwt@celece.ucsd.edu

Prof. John E. Crowell 1
Department of Chemistry
University of California at San Diego
LaJolla, CA
Tel: (619) 534-5441
FAX: (619) 534-0058
email: jcrowell@ucsd.edu

Prof. P. Daniel Dapkus 1
University of Southern California
University Park
Los Angeles, CA 90089-1147
e-mail: dapkus@mizar.usc.edu
Tel: (213) 740-4414
FAX: (213) 740-8684

Unless you are a small business invoking your 2 year proprietory rights clause, you MUST state on the front page of your report: Approved for Public Release; distribution unlimited.

ALF Contractor Distribution List	# Copies
D.T.I.C. Bldg # 5, Cameron Station Alexandria, VA 22314	12
Dr. Andrew Freedman Aerodyne Research, Inc. 45 Manning Road Billerica, MA 01821 Tel: (508) 663-9500 FAX: (508) 663-4918 e-mail: aerodyn@mitvma.mit.edu	1
Dr. Asif Kahn APA Optics 2950 NE 94th Lane Blaine, MN 55434 Tel: (612) 784-4995 FAX: (612) 784-2038 e-mail: 70702.2032@compuserve.com	1
Dr. Duncan Brown Advanced Technology Materials, Inc 7 Commerce Drive Danbury, CT 06810 Tel: (203) 794-1100 FAX: (203) 792-8040	1
Dr. Peter Norris EMCORE Corp. 35 Elizabeth Ave. Somerset, NJ 08873 Tel: (201) 271-9090	1
Prof. Joe Greene Dept. of Materials Science and Engineering University of Illinois 1101 W. Springfield Ave. Urbana, IL 61801 Tel: (217) 333-0747	1
Dr. T. P. Smith IBM T.J. Watson Research Center P. O. Box 218, Route 134 Yorktown Heights, NY 10598 e-mail: trey@ibm.com	1
Prof. Robert F. Davis N.C.S.U. Box 7907	1